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FINAL REPORT

for

Electrified Microheterogeneous Catalysis of Inorganic Materials

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## ***Program Objective***

Electrified Microheterogeneous Catalysis (EMC) is a novel electrochemical method in which an electrifying force (potential, current or field) is applied to a low ionic strength dispersion of catalytically active heterogeneous materials to affect organic transformations at low temperatures and in the absence of light or co-oxidants. This investigation involves the evaluation of the EMC method with three families of heterogeneous catalysts: polyoxometalates (POMs, early transition metal oxides), semiconducting metal oxides and humic acid with a model sulfide, tetrahydrothiophene (THT). This research program had four major goals: 1) To compare the reaction rates and product selectivities of conventional chemical and photochemical catalysis with the EMC method. 2) To investigate the suitability of EMC in the degradation of environmentally hazardous materials and the selective, high yield formation of industrially relevant products. 3) To determine the oxidation/reduction mechanisms which occur when heterogeneous materials catalyze organic transformations under high voltage conditions. 4) To determine the fundamental effects of high voltage conditions on suspensions of solid particles of various charges, electronic structures, proton transfer abilities, surface adsorption sites and surface areas.

## ***Approach***

Goal 1. To investigate differences in reaction rates and product selectivities when conventional chemical and photochemical techniques are compared with the EMC technique we studied the reactivity of the model substrate, tetrahydrothiophene (THT) under all three methods. With the polyoxometalate catalysts, conventional and photochemical catalyses were conducted in homogeneous solutions, while the EMC technique was conducted in heterogeneous solutions. For the semiconducting metal oxides and humic acid, all three methods of catalysis were conducted heterogeneously. All catalysis reactions were conducted under a nitrogen atmosphere. Conventional chemical catalysis was conducted in acetonitrile solutions at room temperature and at reflux (82 °C) for 4, 6 and 8 hours, using t-butyl hydroperoxide (t-BuOOH) as the co-oxidant. Photochemical catalyses were also conducted using acetonitrile as the solvent and t-BuOOH as the oxidant. The light source (a 60 watt spotlight) caused the solutions to reflux and again, reactions were run for 4, 6, and 8 hours. EMC catalysis was conducted for 1 hour at 60 V, using a N<sub>2</sub>(g) flow of 256 ml/min to suspend the particles in an aqueous environment. No co-oxidant, electrolyte or light was added to 0 °C catalyses reactions run under the EMC reactions.

Goal 2. To investigate suitability of EMC in the degradation of environmentally hazardous materials and the selective, high yield production of industrially relevant products, we chose THT as our model substrate. THT was chosen for three reasons: (1) The oxidation of THT is of practical importance in environmental decontamination. The selective oxidation of prominent chemical warfare agents such as mustard or HD is a major governmental concern and this oxidation, as a model for those compounds, addresses the viability of this technique to destroy such harmful chemicals. Additionally, the removal of sulfur containing products (sulfur contaminants) from fuel feedstocks would result in a practical method of improving industrially relevant products (gasolines and motor oils). (2) The products of the oxidation are generally simple (tetrahydrothiophene sulfoxide (THTO) and tetramethylene sulfone (THTO<sub>2</sub>)) and are readily quantified; thus the product yields and distributions of this catalysis are readily obtained by undergraduate or graduate students in an academic setting. (3) THT has been used in previous catalysis studies with POMs and thus the results of EMC method can be readily compared and evaluated.

Goal 3. To determine the oxidation/reduction mechanisms which occur when heterogeneous materials are used to catalyze organic transformations under high voltage conditions, semiconducting metal oxides (such as TiO<sub>2</sub> (anatase and rutile)) and humic acid will be used. Semiconducting metal oxides have been shown to contain four types of absorption sites where each absorption site has a different electron transfer rate. These differences in energy of the electron exchange matrix elements and the level position of the semiconductors were used to make comparisons regarding the effect of the electric field on the catalysis mechanism. Humic acid was investigated as a catalyst so that fundamental proton exchange under high electric fields can be better understood. Structural variation studies on solid state binary oxides which have chain structures, layer structures and three-dimensional structures suggested the type of heterogeneous surface which is required for oxidation/reduction of specific organic substrates.

Goal 4. To determine the fundamental effects of high voltage conditions on suspensions of solid particles, catalysts with various charge, surface and surface area properties were used. POMs were chosen due to their stability to oxidation, their relevance to photochemical and chemical oxidation reactions, and their availability and modifiability. POMs have been used in

photochemical reactions to catalytically functionalize alkanes and dehalogenate environmental toxins. Our program incorporated the use of three different POMs - of various overall charges and framework compositions. These materials represent a large range of surface properties and thus the data from these studies enabled us to make conclusions regard to the interaction between the catalyst surface and electrode, substrate and/or products of the oxidation/reduction.

## Results

Goal 1. Our comparison of catalysis methods has indicated that the order of reactivity is: EMC >> photochemical  $\approx$  chemical at elevated temperatures > chemical at room temperature. Notably, during the oxidation of THT a *one hour* reaction under EMC conditions yielded a 3-fold improvement in the amount of tetrahydrothiophene sulfoxide (THTO) and a 7-fold improvement in the yield of tetramethylene sulfone (THTO<sub>2</sub>) when compared to a *four hour* reaction performed under the next best method - that of photochemical catalysis. Thus, the calculated rate enhancements for THT oxidation with EMC that are 12-60 times that of chemical and photochemical methods.

Goals 2 and 3. Our product analysis for the oxidation of THT has been used to help determine the mechanism of oxidation under high voltage conditions. While normally the products of THT oxidation are restricted to the sulfoxide (THTO) and sulfone (THTO<sub>2</sub>), the EMC method produced a number of novel and previously unreported reaction products. With EMC, we have confirmed the formation of 2,3-dihydro-thiophene and 2-ethylthiophene. Notably, the formation of the latter indicates that either C-S or C-C bond cleavage is occurring during the catalysis reaction. Such bond cleavages have important ramifications in the desulfurization of fuels to reformulate and sweeten gasoline, as well as in the destructive elimination of sulfur compounds used as chemical warfare agents (eg. mustard gas, HD). We will continue to analyze the products of EMC catalysis to determine the total reaction mass balance (additional products such as butane, ethane and elemental sulfur are expected) and to further develop the mechanism of oxidation/reduction and desulfurization under high voltage conditions.

Goal 4. We initiated studies to contrast several classes of heterogeneous catalysts specifically: POMs, semiconducting metal oxides, and humic acid. Our results show that humic acid, a major component in soils, is the best catalyst for THT oxidation and thus, our preliminary data indicates that proton transfer ability, not electronic structure or adsorption sites is the most important factor in THT oxidation. These results will guide our further efforts to optimize the catalyst and will provide a screening method for evaluating future catalysts.

## Conclusions

- 1) The reaction rates of the EMC method are 12-60 times faster than conventional chemical and photochemical catalysis.
- 2) In terms of product distributions, the EMC method competes well against conventional methods for the oxidation of organic sulfides. This indicates that EMC is a viable method for the removal of environmental toxins.
- 3) Preliminary results indicated that, in addition to the production of normal oxidation products, the EMC method produces C-S and/or C-C bond cleavage products from the organic sulfide. These products indicate that sweetening and increased production of fuel feedstocks may be possible with EMC methods.
- 4) Of our three trial catalysts, humic acid (a major component of soils), is the best catalyst for THT oxidation. This data indicates that proton transfer ability, not electronic structure or adsorption sites is the most important factor in THT oxidation using EMC methods.

## ***Significant Publications/Presentations***

### ***Invited Presentations***

1. C. A. Bessel, D. R. Rolison, "Redox Activity of Zeolite-Encapsulated Transition Metal Complexes and Metal Aggregates," 30th Middle-Atlantic Regional Meeting of the American Chemical Society, Villanova University, Villanova, PA, May 22-24, 1996 .
2. C. A. Bessel, "Catalysis with Inorganic Materials," Departmental Seminar Program, Villanova University, Villanova, PA, November 7, 1995.
3. C. M. Meyers, J. P. Dunn, C. A. Bessel, "Catalysis in Unconventional Media," Department of Chemistry, Gettysburg College, Gettysburg, PA, September 26, 1996.
4. C. M. Meyers, J. P. Dunn, C. A. Bessel, "Catalysis in Unconventional Media," Department of Physics, Villanova University, Villanova, PA, November 14, 1995.

### ***Submitted Presentations***

1. C. J. Meyers, J. D. Dunn, C. A. Bessel, "Catalysis in Unconventional Media," Inorganic Chemistry Gordon Conference, New England College, Concord, NH, July 21-26, 1996.
2. C. J. Meyers, C. A. Bessel, "Zeolite Catalysis in Supercritical Fluids," Sigma Xi Poster Contest, Villanova University, Villanova, PA, April 19, 1996.
3. C. J. Meyers, C. A. Bessel, "Electrified Microheterogeneous Catalysis with Inorganic Materials," Mendel Hall Open House, Villanova University, Villanova, PA, February 23, 1996.
4. J. P. Dunn, C. J. Meyers, C. A. Bessel, "Research Report for Summer 1996", Chemistry Department Professional Development Seminar, Villanova University, Villanova, PA, October 24, 1996.